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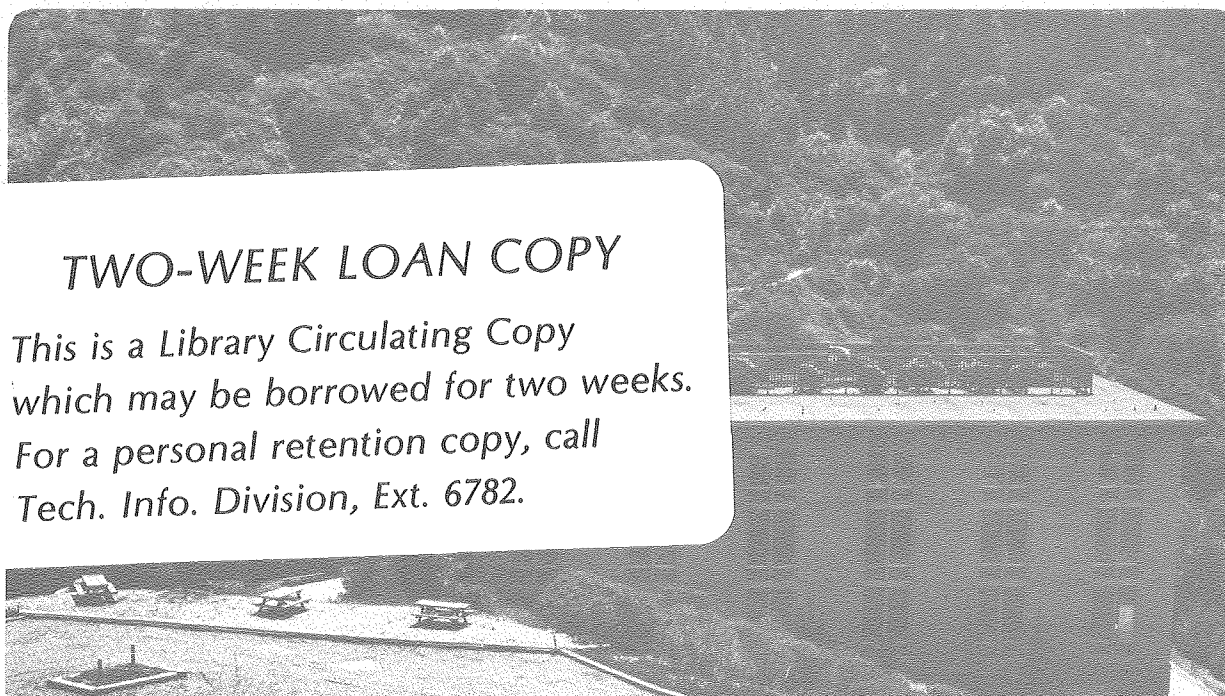
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The Use of Isotope Crossover Experiments in Investigating Carbon-Carbon Bond Forming Reactions of Binuclear Dialkyl Cobalt Complexes

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Biographical sketch. Robert Bergman was born in Chicago in 1942. He received a B.A. degree from Carleton College in 1963, and his Ph.D. with Jerome A. Berson at the University of Wisconsin in 1966. Following postdoctoral work with Ronald Breslow at Columbia University, he joined the faculty of the California Institute of Technology in 1967. He accepted his current position as Professor of Chemistry at Berkeley in 1977, and moved there with his research group in 1978.

Our present understanding of the mechanisms of organometallic reactions stems almost completely from investigation of complexes containing only one metal.[1a,b] Recently interest has been increasing in the synthesis, structure elucidation and reaction mechanisms of polynuclear clusters, complexes containing more than one metal.[1c-e] This attention derives partially from the possibility that polynuclear catalysts and reagents might be designed in such a way that the metals could interact, generating cooperative systems which might be much more selective than their mononuclear analogs. Another stimulant to this work has been the relationship of cluster complexes to larger multi-metal systems, such as heterogeneous catalysts.

Many polynuclear clusters have been prepared and characterized, and some of these have been found to function as unique catalysts or catalyst precursors. However, very little is yet known about how chemical transformations take place at multinuclear reaction centers. Given this paucity of information, we decided a few years ago to initiate mechanistic study of simple cluster systems containing two metal centers, in which each of the metals has a σ-bound organic ligand attached to it. We also chose to focus on reactions of these complexes in which new carbon-carbon or carbon-hydrogen bonds are formed. This Account describes our work on such a system: a binuclear alkyl cobalt complex capable of transferring both alkyl groups to a molecule of carbon monoxide. In this work we have adopted as one of our highest priorities the determination

of whether the cluster "holds together" during its reactions, a
question that is in our opinion too often ignored in such studies.
We have found that isotope crossover experiments provide a powerful
tool for investigating this structural integrity question, and in
this Account we outline a number of examples in which such crossover
experiments have provided important, and occasionally surprising,
information about the mechanisms involved in the reactions of
binuclear cluster complexes. Also summarized are studies of the
reactions of related mononuclear complexes which have provided
information critical to understanding the chemistry of these
binuclear systems.[2]

I. Reactions of η^5-cyclopentadienyldimethyl(triphenylphosphine)cobalt.

The title complex (1) is a well-charzcterized material[3] which
contains two simple alkyl groups bound to cobalt. It undergoes
clean C-C bond forming reactions with a number of unsaturated organic
compounds. Based on our own results in this system and carbonylations
studied extensively in other organometallic complexes,[4] the most
straightforward process of this sort is the reaction of 1 with

carbon monoxide. At 50°C this leads to a quantitative yield of acetone, along with $CpCo(CO)_2$ and $CpCo(CO)PPh_3$ (6). The first step of this reaction, as shown in Chart I, involves replacement of phosphine by CO in the cobalt coordination sphere. Intermediate 4a builds up to some extent and can be detected by NMR and IR spectroscopy. The next step involves migration of CH_3 to coordinated CO, leading to acyl complex 5, and this complex undergoes reductive elimination. We believe the initial replacement reaction proceeds through 16-electron species 2; this intermediate can be scavenged efficiently by phosphines such as $P(CH_3)_3$, which are more nucleophilic than PPh_3. Kinetic studies show the trimethylphosphine reaction is a dissociative process, proceeding via intermediate 2, and by analogy we assume the conversion of 1 to 4a is dissociative as well. Carbonylation of a 50:50 mixture of 0.05M 1 and $1\text{-}d_6$, containing completely deuterated methyl groups, leads to acetone-d_0 and acetone-d_6 containing $\leq$ 1% acetone-d_3, demonstrating the insertion and reductive elimination to be $\geq$ 98% intramolecular.[5]

Complex 1 also reacts with alkynes and alkenes. Charts II and III summarize results from two reactions we have studied particularly extensively.[6,7] Treatment of 1 with excess diphenylacetylene gives alkenes 7 and 8 and metallacycle 9. As in the CO case, this process apparently involves initial replacement of phosphine by alkyne, followed by sterospecific cis insertion of the alkyne into one of the cobalt-methyl bonds, leading to vinyl complex 10. Reductive elimination and scavenging of the unsaturated cobalt fragment leads to 7 and 9, presumably via cobalt π-complex 11. Competitive with displacement of 7 from 11

is insertion of the metal into an allylic C-H bond of the complexed
alkene; this gives a π-allylcobalt hydride (12), which after a second
reductive elimination leads ultimately to isomerized alkene 8. In
the case of ethylene, as shown in Chart III, insertion in π-complex 13
yields propyl/methyl complex 14. β-elimination rather than reductive
elimination is the most rapid process here, and methane and propene
are the organic products.

We have again used isotope labeling, in both crossover and
direct analysis experiments, to provide evidence in support of the
mechanisms outlined in Charts II and III. Reactions carried out with
mixtures of 1 and 1-d_6 demonstrated the alkyne dialkylation to be intra-
molecular. The reaction of 1-d_6 with ethylene proved to be particularly
important, because of a recent suggestion that such apparent insertion
reactions might proceed by α-elimination mechanisms.[8] Reaction of
1-d_6 with ethylene gave only CD_3H and $CD_3CH=CH_2$, a result which
conclusively rules out the α-elimination process in this case.[7]

II. Thermal Decomposition of Binuclear Cobalt Dialkyls.

It is becoming increasingly clear that cluster complexes can
mediate many organic transformations. A crucial question in such
reactions is whether the cluster is the true catalyst or reagent, or
whether it fragments into smaller, transient species which are the
active species.[2,9] Our studies in the binuclear cobalt series provided
a means of examining this question for one system in some detail.

This study began with the largely serendipitous synthesis of a series of binuclear cobalt dialkyls. We found that chemical reduction of $CpCo(CO)_2$ led to the paramagnetic binuclear radical anion 15 (Chart IV), whose structure we determined by X-ray diffraction.[10] Alkylation of the anion was successful with a number of primary alkyl halides. The mechanism of this process is still not clear, but it provided us with the series of neutral dialkyl complexes 16. Both thermal decomposition and carbonylation of 16a led to acetone in high yield.[11] The fact that this was a process initiated in a binuclear complex, and involving the formation of two new C-C bonds, greatly stimulated our interest.

Our work has focused on three complexes in the series, 16a, b and c. We first determined that thermal decomposition of the di-methyl complex led to acetone in 85% yield; the organometallic products of this reaction were CO-deficient cobalt carbonyl complexes which had appeared earlier[12] in the photochemical decomposition of $CpCo(CO)_2$. Monitoring the decomposition by NMR revealed an intermediate which built up and then disappeared during the course of the reaction.[11] This material was identical to the mono-nuclear complex $CpCo(CH_3)_2CO$ (4a) which we had identi-fied as the intermediate responsible for acetone formation during the carbonylation of the mononuclear complex 1. Thus it was clear that transfer of a methyl group from one cobalt atom to the other in 16a preceded ketone formation. In this case, however, cross-over experiments revealed that the reaction was inter- rather than intramolecular. Carbonylation of a mixture of 16a and its methyl-

labeled analog $16a$-d_6 gave an essentially statistical ratio of acetone-d_0, -d_3, and -d_6. When separate solutions of $16a$ and $16a$-d_6 were allowed to decompose until a maximum amount of $4a$ was observed, and then mixed, a much smaller amount of acetone-d_3 was observed. This was consistent with our determination that carbonylation of 1 was intramolecular, and demonstrated that the intermolecular component of the decomposition of $16a$ had to occur before complex $4a$ was formed.

Thermal decomposition of the diethyl complex $16b$ was more complex. Ketone formation, leading to 3-pentanone, occurred, but a competitive β-elimination reaction, leading to ethylene and ethane, was also observed. More enlightening was the decomposition of the bis-trifluoroethyl complex $16c$ shown in Chart V. This led to CpCo(CO)$_2$, cluster, and CpCo(CO)(CH$_2$CF$_3$)$_2$ ($4c$). Due, presumably, to the strength of the metal-carbon bonds in this complex, $4c$ is unusually stable. Unlike $4a$, it does not undergo CO insertion/reductive elimination leading to ketone, and hence may be isolated and characterized by conventional means.[13] As in the case of $16a$, the decomposition of $16b$ and $16c$ also exhibit good first-order kinetics (Table 1).

The first mechanistic hypothesis we constructed to account for these observations is summarized in Chart VI. We postulated that complex 16, in analogy to other complexes with single metal-metal bonds,[14] was in equilibrium with a small amount of monomeric Co(II) species 18. Transfer of a methyl group from one molecule of 18 to another directly generates the NMR-observable intermediate 4, which is isolable in the case of $16c$. This proceeds to ketone by the route outlined earlier in Chart I. Initially we considered[11] a variant of this mechanism in which 18 transfers an alkyl group to

another molecule of 16, generating a chain process leading to 4a. However, the clean first-order kinetics we have since measured for these reactions makes the non-chain mechanism seem more reasonable.

An important part of this mechanism is the first step, involving metal-metal bond cleavage. We therefore set out to obtain independent evidence for this process. Suggestive evidence that this reaction was occurring rapidly at room temperature was provided by some of the chemistry of complexes 16. For example, 16a reacted with NO to give $CpCo(NO)CH_3$, and 16c reacted with I_2 to give a quantitative yield of the isolable complex $CpCo(CO)(CH_2CF_3)I$. More striking, however, was the NMR behavior of 16c. This exhibited reversible broadening of its sharp proton resonances between -50° and +10°, indicating rapid equilibration of 16c with a paramagnetic species, presumably 18c. Once again, a crossover experiment was instrumental in confirming this conclusion: mixing 16a and 16c rapidly generated the unsymmetrical complex 17 (Chart VII). These results provide strong evidence that 16 and 18 are in equilibrium in solution.[13,15] However, they do not tell us whether these Co(II) species--or, for that matter, any intermolecular pathways--are directly involved in the ketone-forming reaction. This question is addressed later in this Account.

III. Carbonylation of Binuclear Cobalt Dialkyls.

Carbonylation of complexes 16 is both cleaner and more rapid than thermal decomposition, and in the case of the dimethyl and diethyl complexes, leads to improved yields of ketone. In the case of 16b, β-elimination is suppressed and ketone formation becomes the

exclusive process observed. The simplest reaction is exhibited by
16c. Carbonylation gives a quantitative yield of CoCo(CO)$_2$ and 4c,
and the reaction is complete in 15 minutes at room temperature.
This result is clearly consistent with the thermal decomposition of
16c, assuming the unsaturated cyclopentadienylcobalt fragments which
formed clusters in the absence of CO are diverted completely to
CpCo(CO)$_2$ in its presence.

Some surprising observations were made on carbonylation of 16a
and 16b. These reactions were more rapid than the thermal decompositions,
and monitoring them by NMR spectrometry allowed us to detect inter-
mediates which did not appear in the thermal decomposition.[16] In the
case of the dimethyl complex 16a, for example, CpCp(CO)$_2$ and
CpCo(CO)(CH$_3$)$_2$ were observed, but at least three new species also
appeared. We believe two of these are the cis and trans diacetyl
complexes 20a and 21a shown in Chart VIII. These materials could be
isolated by low-temperature chormatography, and were pure by NMR
criteria, but their thermal instability prevented our obtaining good
elemental analyses. During the course of the carbonylation a new
metal-bound methyl signal grew into the NMR spectrum and then dis-
appeared. A new acyl signal was also associated with this resonance, and
we believe this material to be the partially carbonylated complex 19a.
Carbonylation of diethyl complex 16b behaved similarly. Although the
monopropionyl complex could not be detected in this experiment, once
again a mixture of two isomeric propionyl dimers (20b and 21b) was
observed and isolated by low-temperature chromatography. Allowing the

carbonylations to proceed at room temperature eventually converted all these materials quantitatively to ketones and CpCo(CO)$_2$.

Studies of the rates and products of decomposition of isolated diacyl complexes 20 and 21 are interesting with regard to the mechanism of ketone formation in these reactions. We have found: (a) decomposition of 20a/21a gives acetone and 20b/21b gives 3-pentanone, both quantitatively in the presence of carbon monoxide; (b) decomposition of a 50:50 mixture of the diacetyl and dipropionyl complexes gives a 1:2:1 ra tio of acetone, 2-butanone, and 3-pentanone, indicating that the reaction is intermolecular, as was determined using isotope crossover experiments for the decomposition of 16a; (c) the conversion to ketone is surprisingly rapid, proceeding at reasonable rates at 0° in THF-d$_8$. Decomposition in the absence of CO gave similar results, except that some cobalt clusters were observed as final organometallic products in addition to CpCo(CO)$_2$. The rates of decomposition are once again first order in acyl complex and show essentially no sensitivity to changes in CO pressure;[16] the rate constants are given in Table I. Most intriguing is the fact that conversion of the diacetyl complexes to acetone occurs substantially more rapidly than the mononuclear complex 4a reacts under the same conditions. This requires that 16a, and presumably 16b, are converted to ketone by two distinct routes--one slower path which proceeds through 4 and another more rapid process, involving diacyls 20 and 21, which completely bypasses 4.

The mechanism outlined earlier in Chart VI can be modified in a relatively straightforward way to explain these observations, and this is done in Chart IX. The critical assumption of the expanded mechanism

is that in the presence of CO, Co(II) intermediate 18 can be trapped

with CO, leading to 22, in competition with its bimolecular conversion

to the mononuclear dimethyl complex 4. As a 19-electron, or perhaps

a 17-electron, η^3-cyclopentadienyl, intermediate there should be a

strong driving force for CO insertion leading to 23.

Complex 23 accounts for the formation of both 20/21 and 19. It

also explains the rapid production of acetone if it can operate as

a methyl rather than acetyl transfer reagent, in analogy to the

hydride transfer propensity shown by the anionic formyl complexes

of Casey[17] and Gladysz.[18] This leads directly to 24, which is undoubtedly

the same intermediate formed more slowly by CO insertion in 4, and

this material gives acetone by direct reductive elimination. That 23

should be able to do this seems reasonable, because methyl transfer

leaves behind coordinatively saturated $CpCo(CO)_2$, whereas acyl transfer

between two molecules of 23, and methyl transfer between two molecules

of 18, must both generate 16-electron species, and are therefore

slower processes.

IV. Reactions of Bridged Binuclear Dialkyls.

The observations summarized above served to identify a number

of the intermediates involved in the thermal decomposition and

carbonylation reactions of binuclear cobalt dialkyls. They also

convinced us that the scrambling of alkyl groups, initially revealed

by isotope crossover experiments in the decomposition of 16, was

ubiquitous in these decompositions, and occurred at a rate much more

rapid than that of product formation. As indicated earlier, this

raised an important question: is alkyl group scrambling a process

actually located on the path to ketone product, or is it a

side reaction which simply produces completely scrambled starting

material, which then proceeds on to ketone by an intramolecular

mechanism? Our further experiments, described below, provide strong

evidence that scrambling and ketone formation result from the

same process.

In order to answer this question, we decided to prepare and

examine the chemistry of bridged complex 28. We reasoned that the

28 $\rightleftharpoons$ 29 equilibrium shown in Chart X would favor 28 more than 16 was

favored in the unbridged case, because of the smaller amount of

translational entropy associated with 29, compared with the two

independent fragments presumably released in the dissociation of 16.

This predicts that conversion to acetone should be slower for 28 than

for 16 if dissociation is in fact the first step on the route to

ketone. Additionally, we thought the forced proximity of the metal

centers in 28 might cause the reaction to be completely intramolecular

in this system.

Bridged complex 28 was prepared from dicyclopentadienylmethane

by the route shown in Chart X. The reactions of 26 and 28 are quite

parallel to those of the parent compounds.[19] Complex 26 is reduced

to radical anion 27, which can be alkylated to give 28. This, in turn,

gives acetone and insoluble cluster complexes on thermal decomposition,

and acetone and 26 quantitatively on carbonylation. Consistent with

our mechanistic hypothesis, these reactions are considerably slower

than those observed with 16. Temperatures near 80° are required to

induce thermal decomposition of 28, and even carbonylation requires

a temperature of 70° to achieve a reasonable rate. Because metal-

metal bond cleavage is now slower, neither complex 30 nor binuclear

diacyl complexes build up during the course of these reactions.

Having determined that the chemistry of 28 is analogous to that of 16, we again carried out crossover experiments to examine the intramolecularity of the carbonylation. Our first studies, carried out at relatively high concentration of starting complex, showed a significant amount of crossover (Table 2). Interestingly, we did not observe a completely statistical ratio of labeled acetones. Furthermore, runs at varying concentrations of 28 demonstrated that the intramolecularity of the process increased at lower concentrations. Because of the linked cyclopentadienyl rings, dissociation-recombination of the metal-metal bond in 28 cannot produce label scrambling. Just to be sure some other scrambling mechanism was not operative, this was confirmed by isolation of 28 after partial reaction and analysis by mass spectroscopy. Therefore, for complex 28 at least, label scrambling in the ketone product is not a result of some completely independent randomization process in the starting material.

The mechanistic hypothesis suggested earlier accounts nicely for this result. One need only assume that, as predicted, metal-metal bond cleavage in 28 gives 29; CO then attacks one of the metal centers in 29, forcing a methyl group to migrate to the other, leading to 30. When the concentration of 29 is high enough, transfer of methyl to a Co(II) center in a different molecule becomes competitive, and this is the concentration-dependent intermolecular component of the reaction. Complex 30 (L = CO) then undergoes insertion/reductive elimination as discussed earlier for related mononuclear complexes, leading to acetone and 26.

However, nature was not about to provide us with such a tidy conclusion. Given the relative stability of 28 and the cleanliness of its carbonylation, we next decided to examine its reaction with phosphines. We had made an attempt to examine the corresponding reaction of 16a; this reaction gave a lowered yield (58%) of acetone, as well as a mixture of mononuclear and cluster complexes[20]; the complexity of this reaction discouraged our attempts to investigate it in detail. In the case of 28, we expected that phosphine would simply replace CO as the methyl-migration-inducing ligand. Thus phosphine, written as "L" in Chart X, would attack one of the metal centers in 29 and force methyl migration as in the CO case, leading to 30 (L = PR_3). This should rapidly give acetone and 31. In the event,[19] reaction of 28 with phosphine was quite clean, proceeding at a reasonable rate even at 25°. However, no acetone was formed in this reaction. As shown in Chart XI, the sole product was the single organometallic complex 32.

The most surprising thing about this result is that complex 32 has both CO groups bound to the same metal atom. In view of this result, we had to question the hypothesis that 29 is the initially formed intermediate, because it is difficult to devise a convincing mechanism to explain why one of the metal-CO bonds broken in the generation of 29 should find a way to re-form. A more reasonable explanation is that both metal-carbonyl bonds at one of the metal centers in 28 remain intact during the entire reaction. Our mechanistic hypothesis must therefore be modified.

As shown in Chart XI, we suggest that only two, rather than three, bonds in 28 are cleaved upon reaction with an entering ligand, leading to 34. This intermediate, although undoubtedly reactive, has two 18-electron cobalt atoms.[21] When L = CO, the two metal centers are chemically identical, and cleavage of either bond a or bond b may occur. When L = phosphine, however, cleavage of bond a is favored because this process places the relatively electron-donating phosphine ligand on the less electron-rich metal center. This leads to 35; transfer of the methyl group then gives the product 32.[22] That this transfer may become intermolecular at high enough concentrations is once again demonstrated by the appropriate crossover experiments (Table 2).

Kinetic studies yielded one further piece of information about the first part of the mechanism of this reaction.[19] Reaction of phosphine with 28 might occur in one step (k_3 in Chart XI). Alternatively, 28 might suffer bond cleavage to give 33, followed by reaction of PR_3 with the 16-electron metal center so generated. These mechanisms are kinetically distinguishable if the latter mechanism obtains and the quantity $k_2[L]$ can be made larger than the recombination rate constant k_{-1}. This is exactly the case for the reaction of 28 with PPh_3. At moderate phosphine concentrations the rate is approximately first order in phosphine. However, as the concentration of PPh_3 is raised, the reaction approaches a limiting rate which is independent of $[PPh_3]$. This is strong evidence for the dissociative mechanism, and from these data one can extract the dissociation rate constant $k_1 = 1.28 \times 10^{-4}$ sec^{-1} and the ratio $[k_{-1}/k_2] = 4.3 \times 10^{-2}$ M^{-1} (25°).

V. Conclusions

It is possible that each of the reactions of 16 and
28 discussed here takes place by independent mechanisms. However,
this assumption seems neither reasonable nor economical. We
suggest instead that the chemistry of these differently substituted
systems are related, and provide insight into a general pattern of
behavior for the ligand-induced decompositions of complexes related
to 16.

In Chart XII we have combined the information obtained on these
related systems into a generalized mechanistic hypothesis, illustrated
for simplicity for only the parent dimethyl complex 16 and the single
ligand CO. As with 28, we assume that metal-metal bond cleavage in
16 also begins by conversion to 36. In the absence of added ligand,
dissociation to 18 may occur, and this overall process is rapid and
reversible at room temperature and below. In the presence of an
external ligand such as CO, 37 is formed. This may dissociate to
one molecule of 18 and one molecule of dicarbonyl 22. Reaction of
these two species with one another gives 4 and
6, and 4 is converted to acetone, presumably via 24, at a moderate
rate at room temperature.

Besides transferring a methyl group to 18, 22 may also undergo
CO insertion to give 23. Reversible dimerization of 23 leads to
isolable binuclear diacyls 20 and 21, and reaction of 23 with 18
gives 19. Alternatively, one molecule of 23 may transfer a methyl
group to another, releasing a molecule of 6 and 24. This provides
a rapid route to acetone which bypasses dimethyl complex 4.

In summary, it is perhaps reasonable to derive the following generalizations from our studies of these binuclear systems. First, the decomposition of 16 and its derivatives is now one of the few carbon-carbon bond forming reactions initiated in a binuclear complex which is understood at a reasonable level of detail. Second, crossover experiments have played a crucial role in delineating credible mechanistic hypotheses in this work; these experiments have taught us that there is often a real possibility that intermolecular mechanisms intervene in processes which we at first naively guess to be intramolecular.

Third, our results re-emphasize the concern that the reactive species in so-called "cluster-catalyzed" reactions might in fact be reactive fragments of lower nuclearity. Finally, in a somewhat more general sense, we have tried to point out in this account how knowledge of the chemistry of mononuclear complexes has been crucial to our understanding of their binuclear relatives. We hope, in turn, that current and future investigations of binuclear systems will provide a base for understanding the chemistry of larger clusters.

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$$\left\{ \begin{array}{l} \text{Fraction of} \\ \text{Intermolecular} \\ \text{Product} \end{array} \right\} = \left[f_{d_3} \right]_p \left(1 + \frac{1}{2}\left[\frac{f_{d_0}}{f_{d_6}} \right]_o + \frac{1}{2}\left[\frac{f_{d_6}}{f_{d_0}} \right]_o \right)$$

$\left[f_{d_3} \right]_p$ = fraction of d_3 acetone product; $\left[f_{d_0} / f_{d_6} \right]_o$ = ratio of d_0 to d_6 starting material.

defined in this way, to the measured percentages of the three labeled acetones. (b) Another facet of this experiment illustrates the need to carry out careful controls in order to properly interpret crossover labeling data, especially in cases where scrambling is detected. Our first experiments on the carbonylation of mixtures of 1 and 1-d_6, carried out using relatively high concentrations of starting complex, gave substantial amounts of acetone-d_3. Lower concentrations reduced the amount of scrambling, and the percentages shown in Chart I are those determined at a starting concentration of 0.05M. The source of the intermolecularity was uncovered by heating complexes 1-d_0 and 1-d_6 in the absence of CO for 24 hr at 60° (the carbonylation temperature) and an

initial concentration of 0.25 M, and then diluting to 0.05 M
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13. M.A. White and R.G. Bergman, unpublished results.

14. See, for example, (a) H.B. Abrahamson and M.S. Wrighton, _J. Amer. Chem. Soc._ $\underset{\sim\sim}{99}$, 5510 (1977); (b) J.P. Fawcett, A. Poë, and K.R. Sharma, _ibid._ $\underset{\sim\sim}{98}$, 1401 (1976); (c) E.L. Muetterties, B.A. Sosinsky and K.I. Zamaraev, _ibid._ $\underset{\sim\sim}{97}$, 5299 (1975); (d) R.D. Adams, D.E. Collins, and F.A. Cotton, _ibid._ $\underset{\sim\sim}{96}$, 749 (1974).

15. A word is appropriate here about two other approaches we have taken to this problem. In principle, one should be able to obtain the type of information obtained in the $\underset{\sim\sim}{16a}$ + $\underset{\sim\sim}{16c}$ reaction by carrying the isotope crossover reaction to partial completion, reisolating $\underset{\sim\sim}{16}$, and analyzing it mass spectroscopically. However, $\underset{\sim\sim}{16}$ exhibits no parent ion, even at low voltages; the ion of highest m/e corresponds to exactly half the molecular weight of $\underset{\sim\sim}{16}$. That the complex is dimeric in solution was indicated by the presence of a normal NMR spectrum showing the complex is diamagnetic, and confirmed by cryoscopic molecular weight experiments.

In a second approach, we have carried out variable temperature ESR studies on $\underset{\sim\sim}{16a}$ and $\underset{\sim\sim}{16c}$. Both exhibit ESR signals in the region expected for Co(II) species (g for $\underset{\sim\sim}{16a}$ is 2.012 and for $\underset{\sim\sim}{16c}$ is 2.124). Unfortunately, however, we were unable to resolve the cobalt hyperfine splitting in liquid solution, even at low temperature. In frozen solution, some hyperfine splitting is seen, but the resolution is still not clear enough to provide truly

definitive evidence that these signals are due to CpCo(R) (CO) species.

16. M.A. White and R.G. Bergman, J.C.S. Chem. Commun., 1979, 000.

17. C.P. Casey and S.M. Neumann, J. Amer. Chem. Soc. 100, 2545 (1978).

18. J. Gladysz and W. Tam, J. Amer. Chem. Soc. 101, 4766 (1979).

19. H.E. Bryndza and R.G. Bergman, J. Amer. Chem. Soc. 101, 4766 (1979).

20. N.E. Schore and R.G. Bergman, unpublished results.

21. A very similar binuclear intermediate, also containing a single carbonyl bridge and no metal-metal bond, was observed recently; cf. D.R. Tyler, M.A. Schmidt and H.B. Gray, J. Amer. Chem. Soc. 101, 2753 (1979).

22. This hypothesis suggests that phosphine ligands comparable in π-acidity to CO might result in the formation of some acetone, since in this case cleavage of bonds a and b should be more competitive. In agreement with this prediction, reaction of 28 with PF$_3$ gives acetone (approx. 10% yield) in addition to a predominant amount of the PF$_3$ analog of complex 32.

Table I

Selected Kinetic Data for Reactions of Mono- and Binuclear Cobalt Alkyl Complexes

Reaction	Conditions, Temp.	Rate Constant (sec^{-1})
16a → Acetone + clusters	THF, 33°	6.7×10^{-5}
4a → Acetone + clusters	THF, 35°	4.5×10^{-6}
16b → {3-pentanone, C_2H_9, C_2H_6, clusters}	THF, 23°	8.18×10^{-5}
16c → 4c + 6 + clusters	THF, 23°	4.07×10^{-5}
20,21 → Acetone + 6	THF, 0.5 atm CO, 0°	5.5×10^{-5}
20,21 → Acetone + 6	THF, 9.5 atm CO, 0°	3.23×10^{-5}
28 + PPh_3 → 32a	C_6D_6 0.10 M PPh_3, 25°	5.59×10^{-5}
28 + PPh_3 → 32a	C_6D_6 0.93 M PPh_3, 28°	1.24×10^{-4}

Table II

Isotope Labeling Data Obtained in Crossover Experiments on the Reaction of Mixtures 28-d_0 and 28-d_6 with CO and PPh_3.

Starting Complex (%) Total Conc. (m)	28-d_0	28-d_6	Entering Ligand	T($^\circ$C)	Acetone Products[c] d_0	d_3	d_6	Molecularity %Intra-	%Inter-
0.25	53	47	CO[a]	70	40	28	32	44	56
0.05	55	45	CO[a]	70	52	5	43	90	10
0.25	46	54	PPh_3[b]	25	38	16	46	67	33
0.05	49	51	PPh_3[b]	25	49	1	50	98	2
0.25	69	31	PPh_3[b]	70	69	3	28	93	7

[a] Toluene solvent [b] Benzene solvent [c] Acetone was obtained as the direct product of the carbonylation reaction and analyzed by mass spectroscopy. In the PPh_3 reaction, product $32a$ was first diluted to a concentration $\leq$ 0.05 $\underline{M}$ and then carbonylated to generate acetone for analysis (the run at 0.05 $\underline{M}$ 28 precludes the possibility of significant label scrambling during the carbonylation of $32a$ at these concentrations; see footnote 5b).
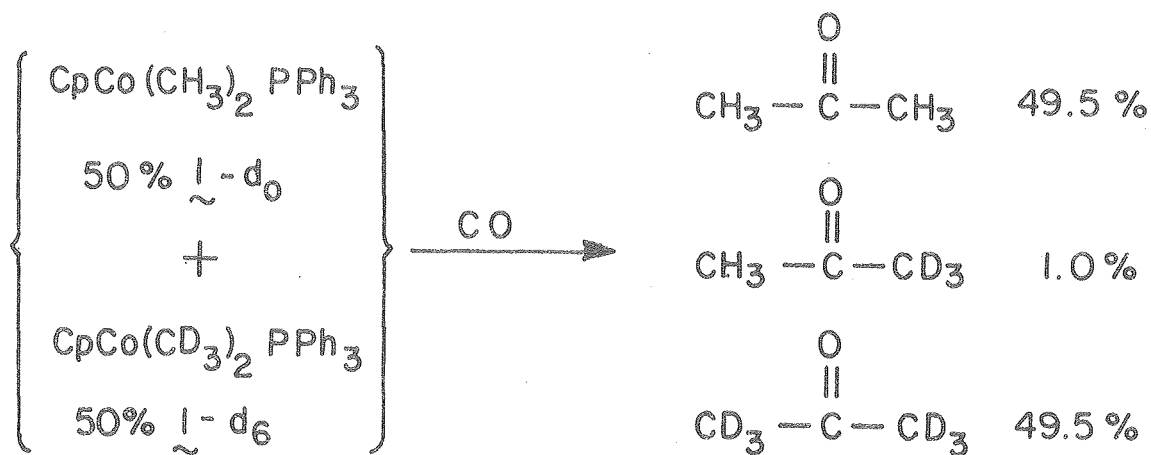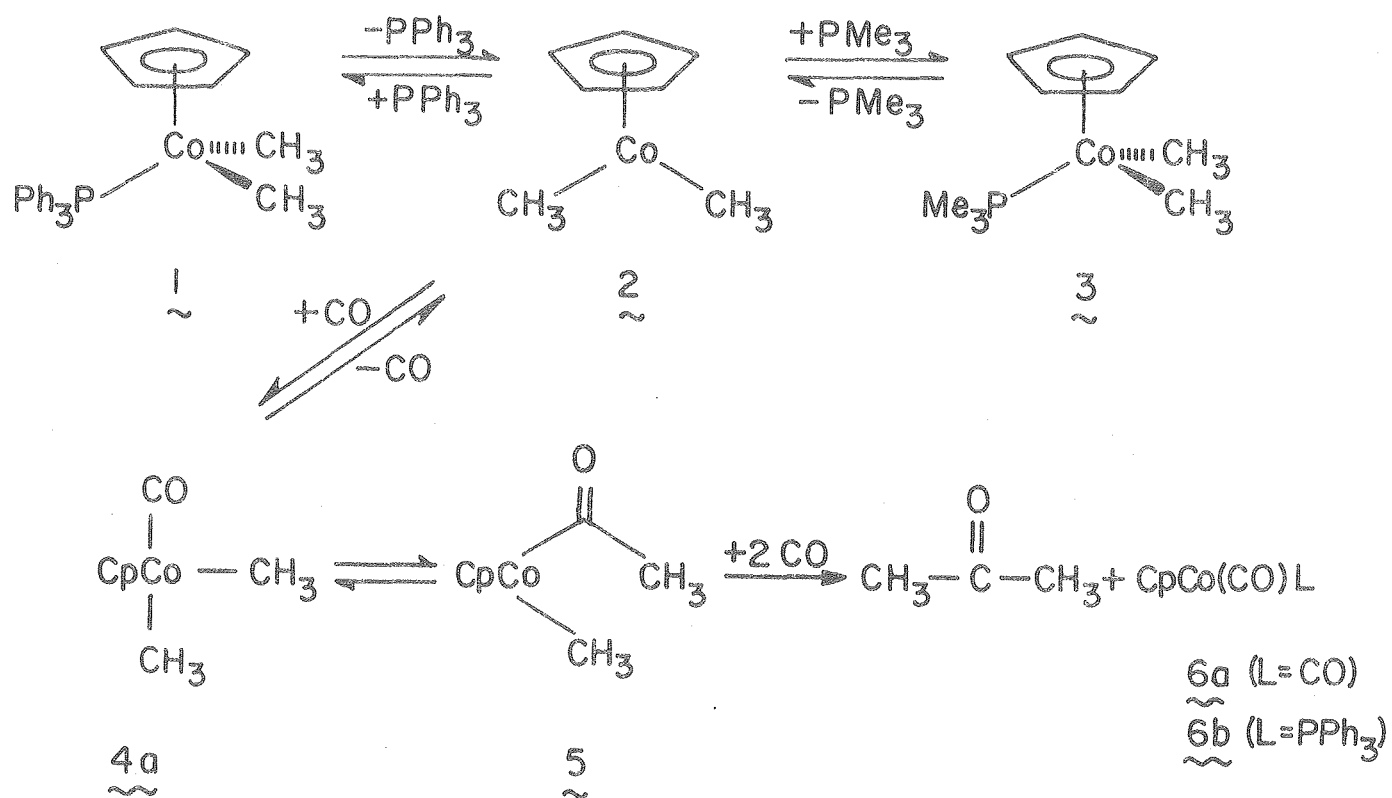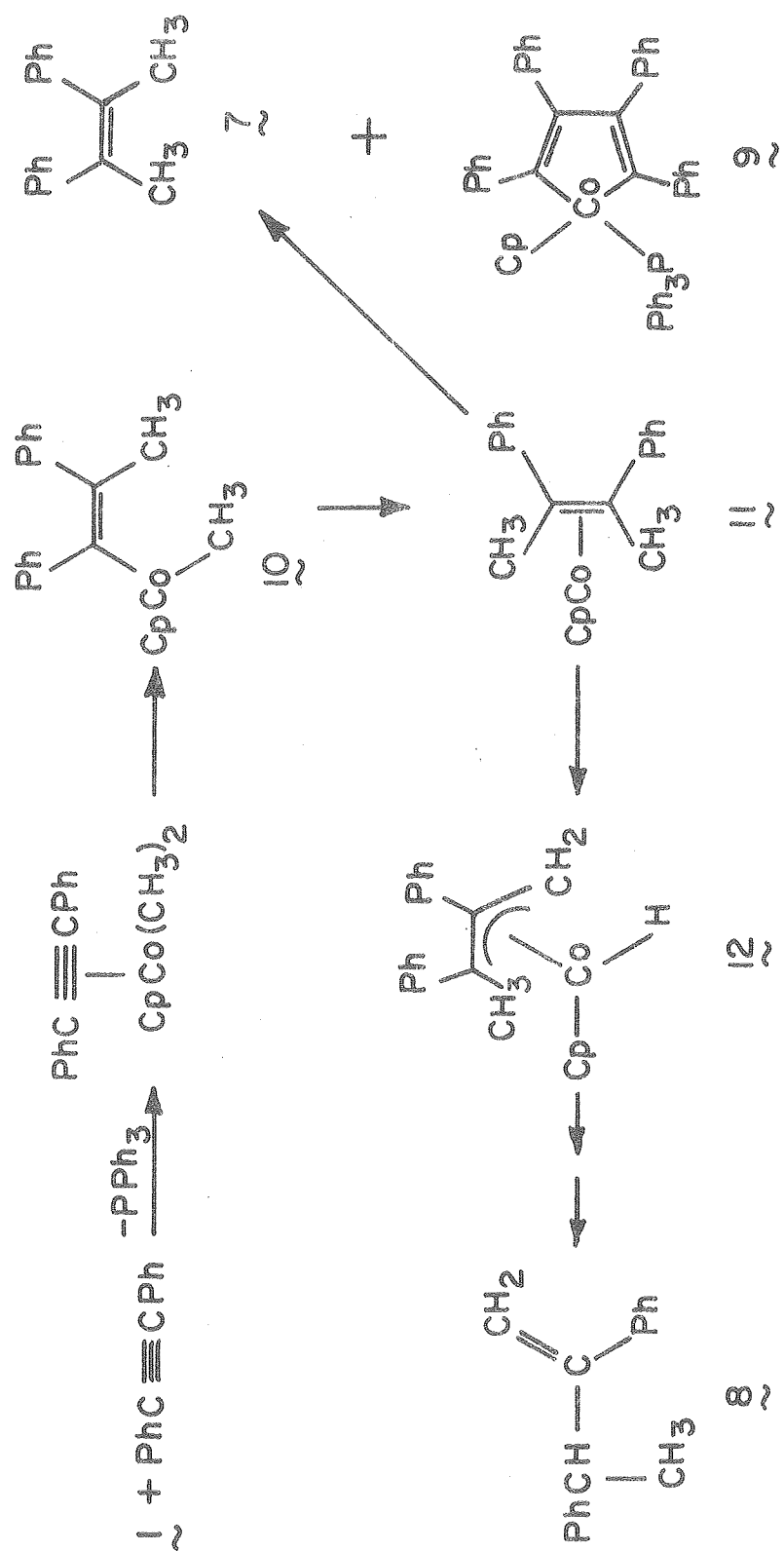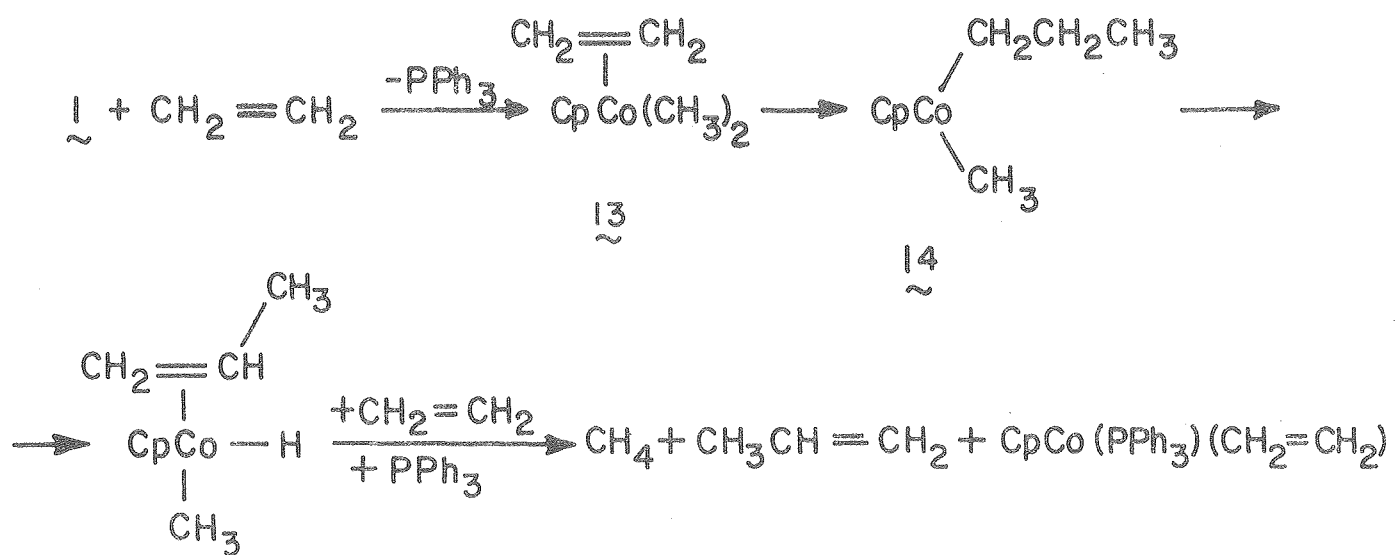
CHART I

CHART II

CHART Ⅲ

$$\underset{\sim}{1} + CH_2 \!=\!\!= CH_2 \xrightarrow{-PPh_3} \underset{\underset{\sim}{13}}{\overset{\overset{\displaystyle CH_2 \!=\!\!= CH_2}{|}}{Cp\,Co(CH_3)_2}} \longrightarrow \underset{\underset{\sim}{14}}{Cp\,Co\!\!\underset{CH_3}{\overset{CH_2CH_2CH_3}{<}}} \longrightarrow$$

$$\longrightarrow \underset{\underset{CH_3}{|}}{\overset{\overset{\displaystyle CH_2 \!=\!\!= CH\!-\!CH_3}{|}}{Cp\,Co}}\!-\!H \xrightarrow[+\,PPh_3]{+\,CH_2\!=\!\!=CH_2} CH_4 + CH_3CH\!=\!\!=CH_2 + Cp\,Co\,(PPh_3)(CH_2\!=\!\!=CH_2)$$

CHART IV

Cp–Co(CO)$_2$ $\xrightarrow{\text{Na}}$ Na$^+$ [(Cp) – Co ⋯⋯ Co – (Cp)]$^\bullet$ $\xrightarrow{\text{R–I}}$
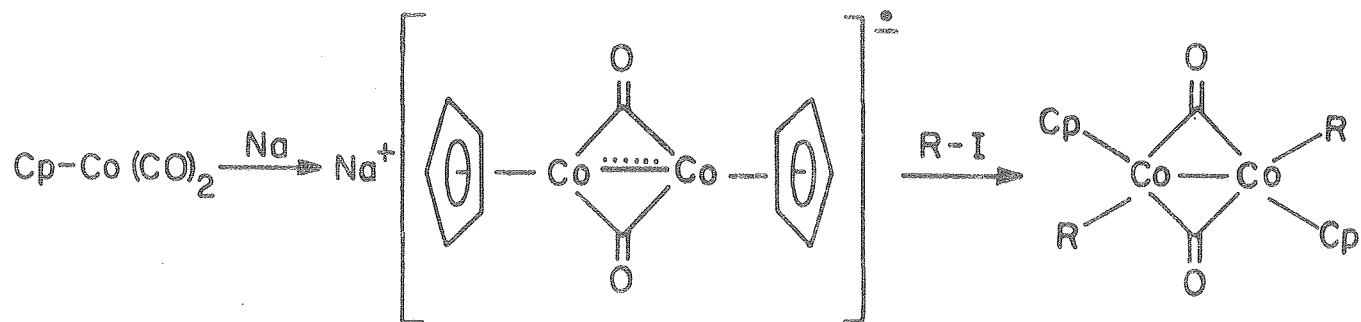
15

16a   R = CH$_3$

16a-d$_6$ R = CD$_3$

16b   R = CH$_2$CH$_3$

16c   R = CH$_2$CF$_3$

$$\left\{ \begin{array}{c} 50\% \quad \text{16a} \\ + \\ 50\% \quad \text{16a-d}_6 \end{array} \right\} \longrightarrow$$

CH$_3$—C(=O)—CH$_3$ 26%

CH$_3$—C(=O)—CD$_3$ 47%

CD$_3$—C(=O)—CD$_3$ 27%

CHART $\underline{V}$

$$16c \xrightarrow[\text{THF-}d_8]{25°} CpCo(CO)_2 + CpCo(CO)(CH_2CF_3)_2 + \text{clusters}$$

$4c$

CHART VI

16 $\rightleftharpoons$ 2 CpCo with R, CO ligands (18)

2 CpCo (R, CO) (18) $\longrightarrow$ $CpCo(CO)R_2$ + "CpCoCO"

$CpCo(CO)R_2$ + "CpCoCO" $\longrightarrow$ clusters

$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$ $\longleftarrow$ 4 $\longrightarrow$ "CpCo" $\longrightarrow$ clusters
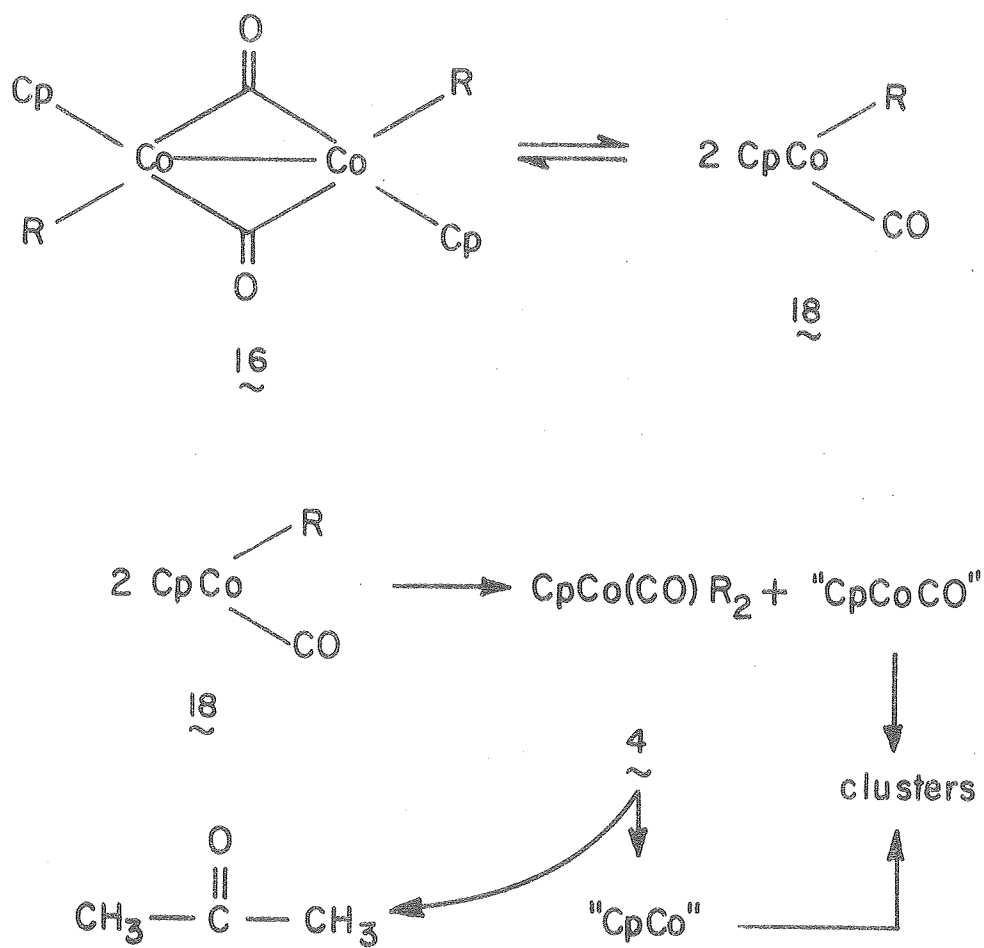
CHART VII

CHART VIII

CHART IX

$$16 \rightleftarrows 2 \; Cp—Co(CO)CH_3$$

$$18 \; \overset{CO \downarrow\uparrow -CO}{}$$

$$22 \; 2 \; Cp—Co(CO)_2CH_3 \rightleftarrows$$

$$20, 21$$

$$4 \; + \; "CpCoCO" \xrightarrow{+CO} CpCo(CO)_2$$

$$\rightleftarrows \; \begin{array}{c} CH_3 \\ | \\ C=O \\ | \\ Cp—Co—CH_3 \\ | \\ CO \end{array} \quad 24$$

$$CH_3—\overset{\overset{\textstyle O}{\|}}{C}—CH_3$$

$$+18 \; 19$$

$$23 \; \begin{array}{c} O \\ \| \\ CH_3—C \\ \quad \searrow Co—Cp \\ OC \end{array}$$

$$23 \; \begin{array}{c} CH_3 \\ | \\ O=C \\ \quad \diagdown \\ Cp—Co \\ \quad \diagup \diagdown \\ \quad \quad CO \end{array}$$

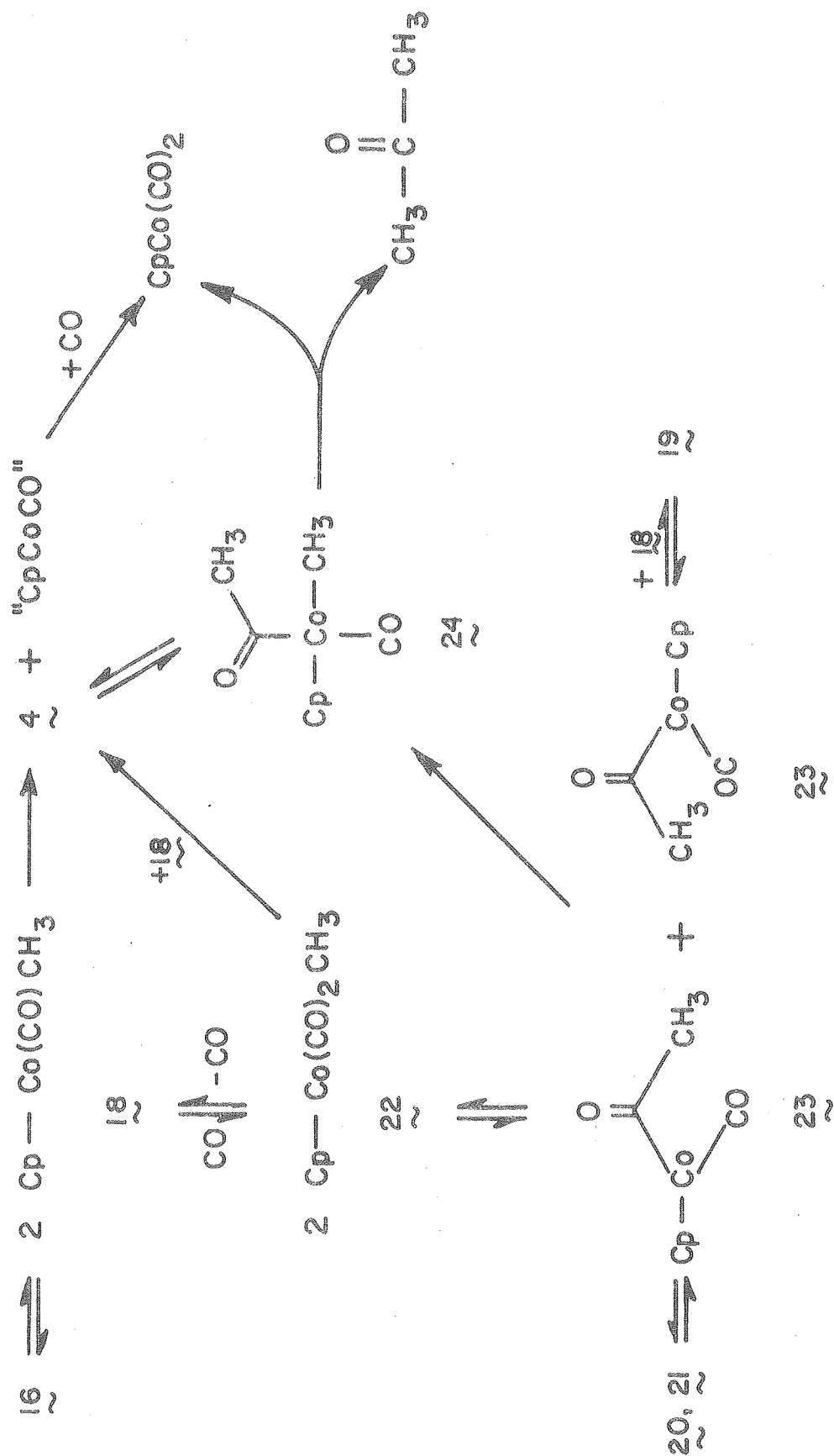CHART X

CHART XI

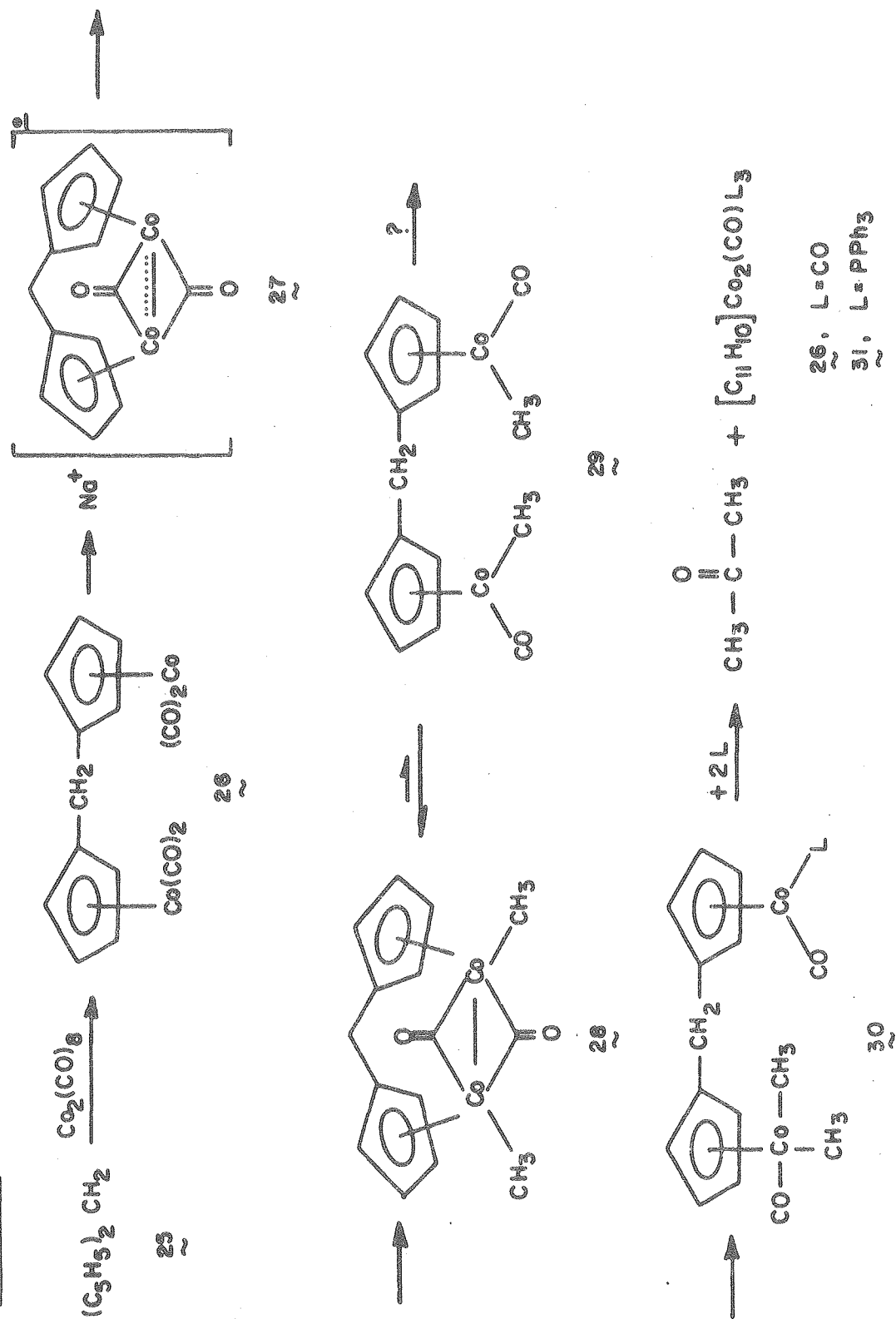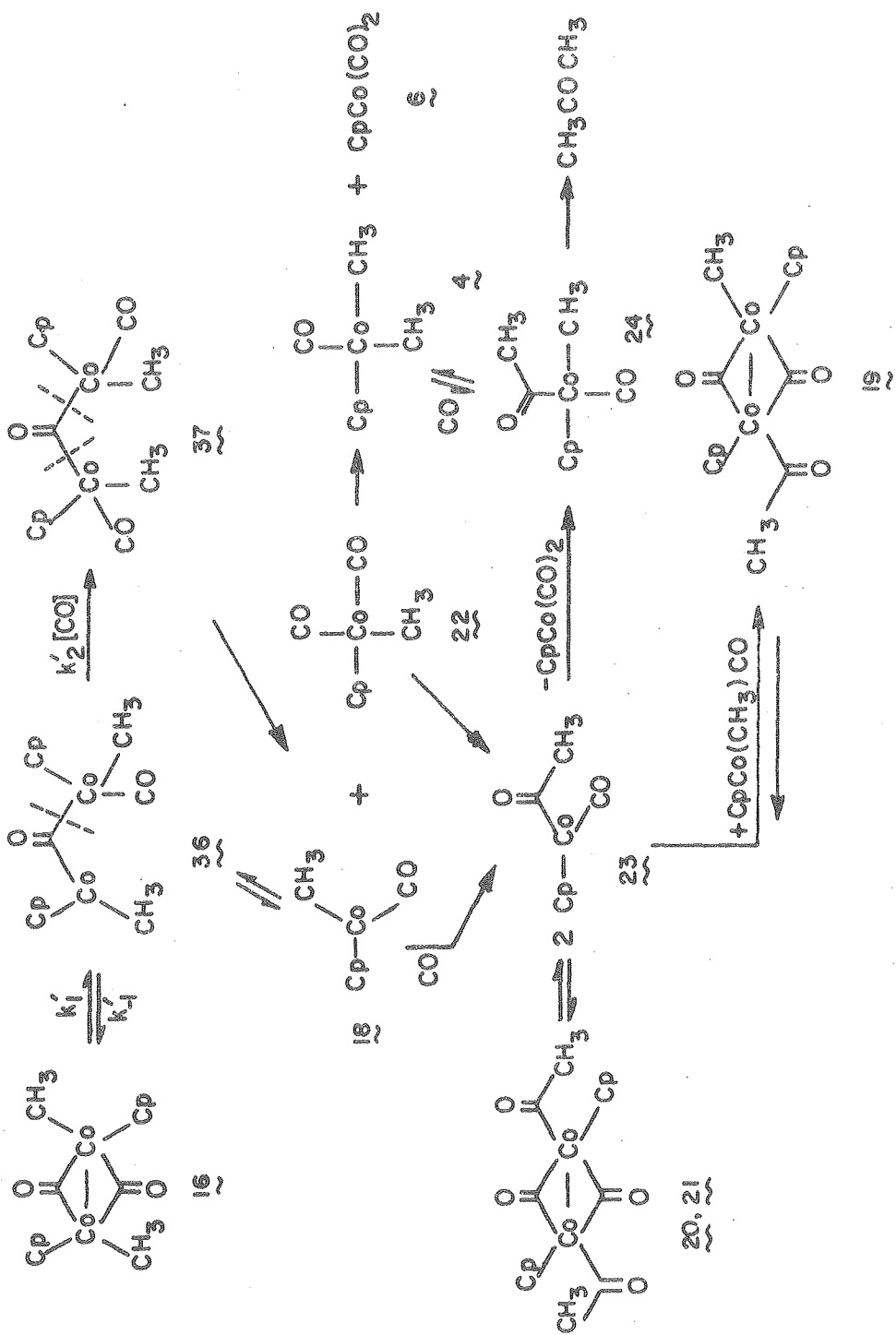32a (L = PPh₃)
32b (L = P(CH₃)₃)
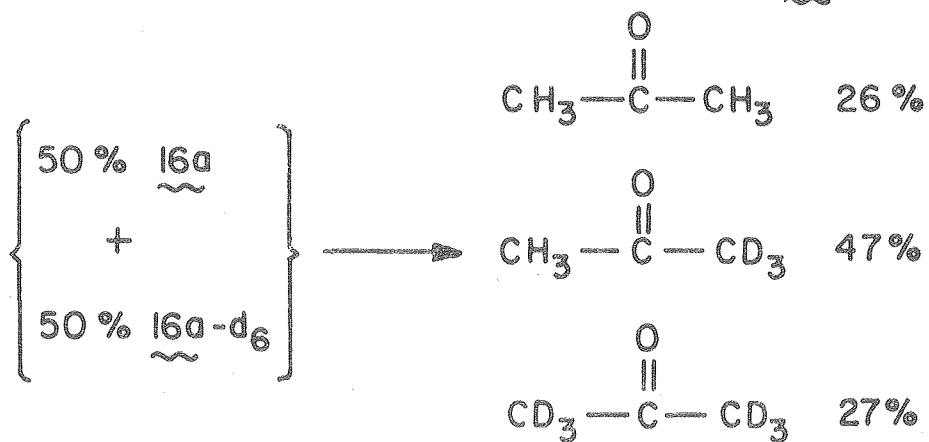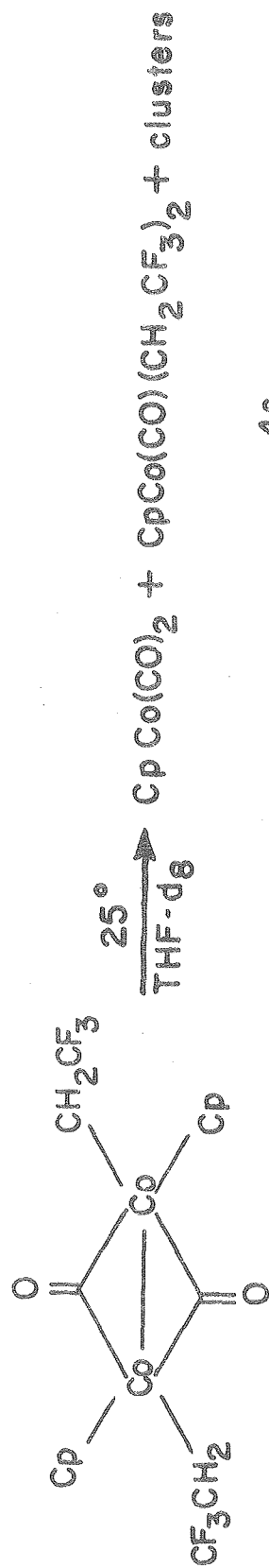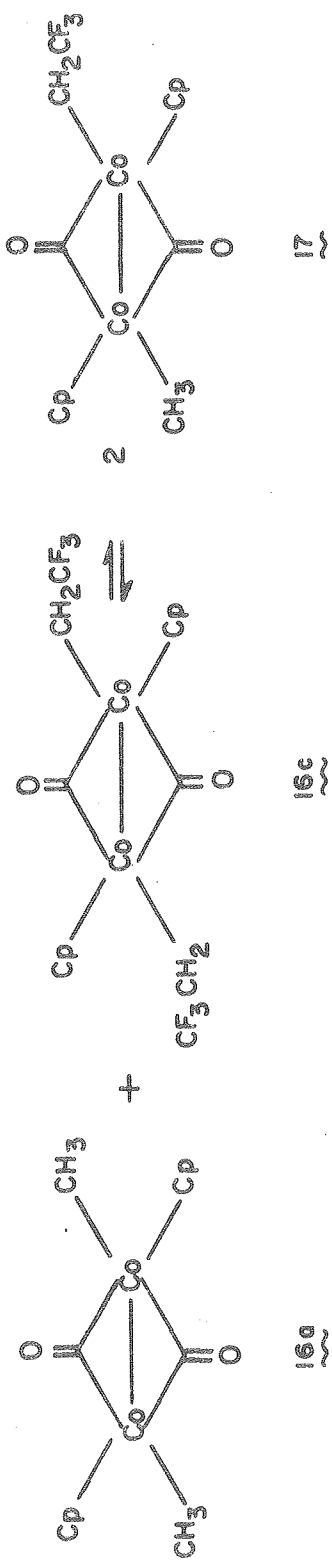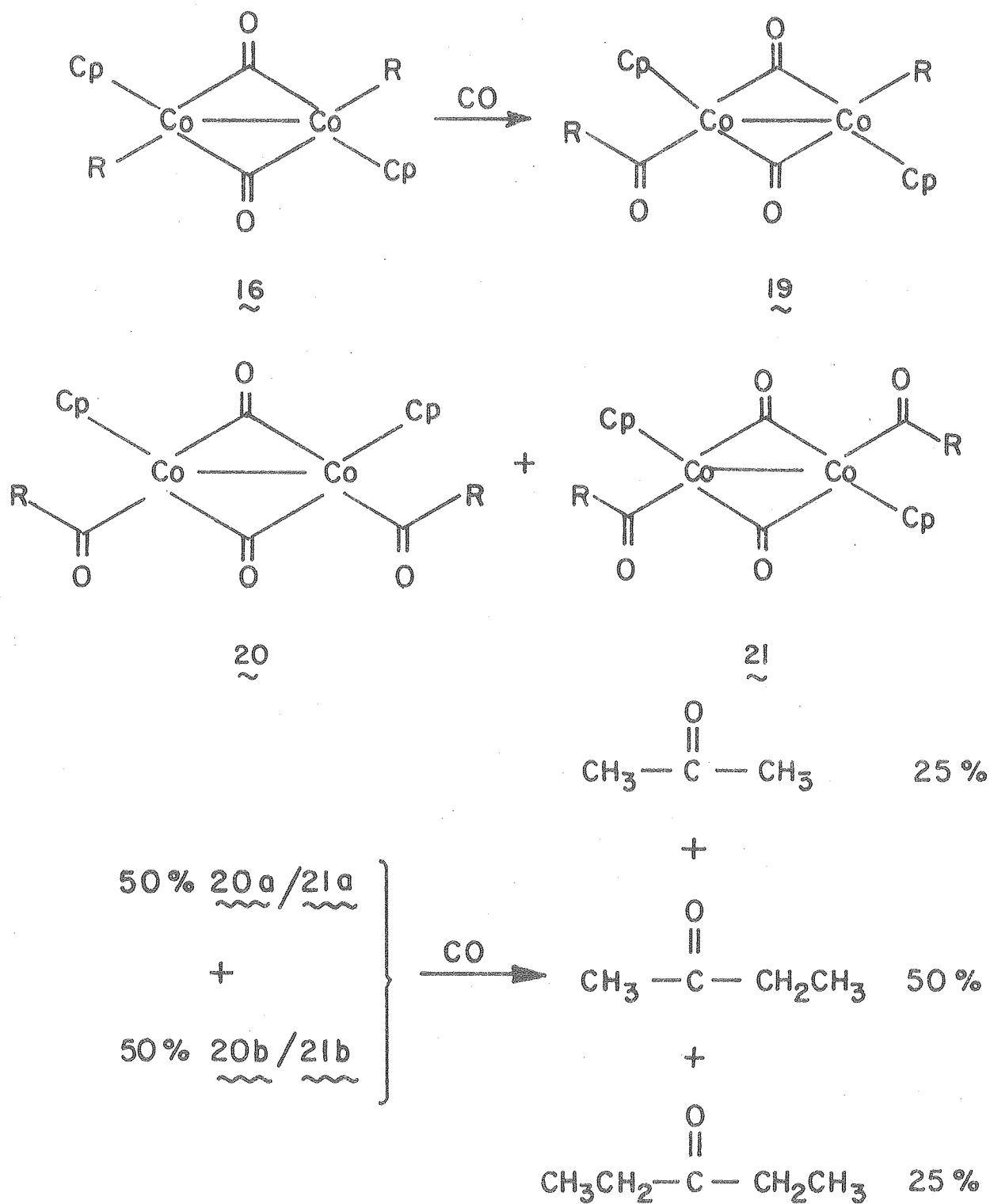
CHART XII

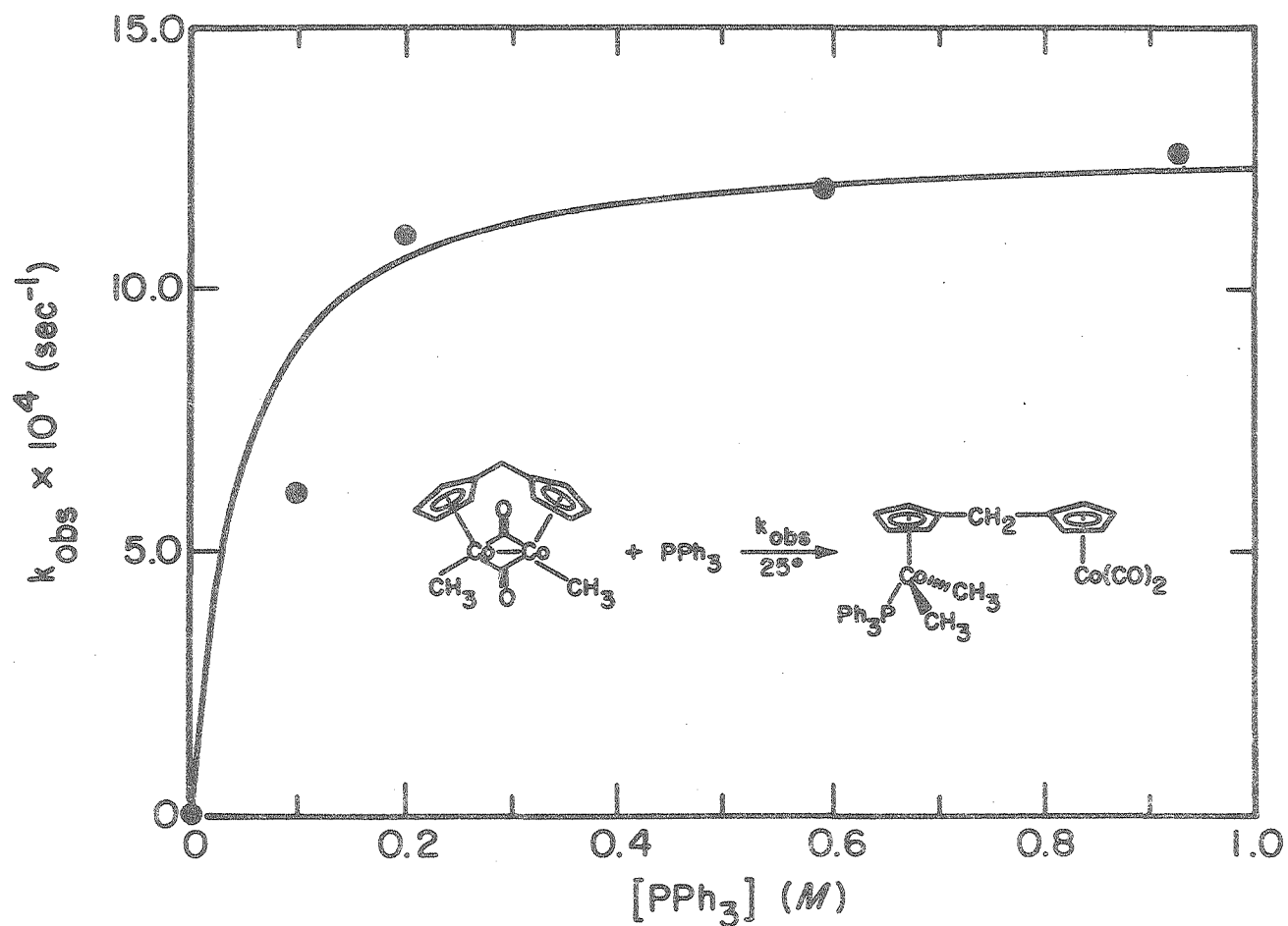<u>Fig. 1.</u> Dependence of the pseudo-first-order rate constant
for reaction of <u>28</u> with excess PPh_3 (benzene-d_6, 25°) upon
the concentration of PPh_3.